

Distillation Studies

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN
THE UNIVERSITY OF MICHIGAN

By
JOHN COLLIN GENIESSE

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PRESENTED TO THE FACULTY OF THE
UNIVERSITY OF LEIDEN
IN CANDIDACY FOR THE DEGREE OF
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BY
J. J. VAN DER WERF



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Distillation Studies¹

By E. H. Leslie and J. C. Geniesse

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A careful study has been made of the performance of an effective specially designed laboratory fractionating column. The apparatus and its operation are described in detail. Thermal efficiencies of all parts of the apparatus were determined as a necessary part of the analysis of its performance. The results obtained by use of the laboratory column were compared with those possible only by use of the hypothetical column of infinite number of equilibrium units.

The characteristics of the system chloroform-toluene are outlined and data necessary for the rapid analysis of these solutions are presented.

The influence of vapor velocity on the effectiveness of the laboratory column was studied. Information so gained, taken together with that secured by critical study

or review of work by others, leads to the conclusion that vapor velocity can be disregarded as a variable factor in column design and operation, provided the velocity is not so high as to cause excessive entrainment or priming.

The suggestion is made, based on data presented, that reflux ratio may also be without influence on the effectiveness of a fractionating column.

The effectiveness of the column packings was found to vary inversely with the diameter, as has previously been shown by Peters.

Charts are presented that show at a glance the relationship of reflux ratio, number of equilibrium units, and change in composition for solutions of chloroform and toluene.

THE object of this investigation was to make a complete analysis of the performance of an effective laboratory distillation equipment and to determine how closely its performance approached that of the hypothetical ideal apparatus of infinite number of equilibrium units and minimum vaporization and reflux. Further objects were to secure data on the effect of vapor velocity in a packed column and on the relative effectiveness of packings of different diameters. Also the preparation of charts to make clear the relationships between reflux ratio and fractionation effected by one equilibrium unit was intended.

Scope of Experimental Work

The experimental work consisted in determining the actual heat, weight of vapor, and reflux ratio required for the separation of 1 gram of practically pure chloroform from chloroform-toluene solutions of four different concentrations. Solutions containing 15, 25, 35, and 50 per cent of chloroform by weight were distilled through the column packed with 5.6-mm. Lessing rings, and 25 and 50 per cent solutions were distilled through the column packed with 6.5-mm. rings. Solutions containing more than 50 per cent chloroform were not used, because it would have been almost impossible accurately to measure the small reflux required. Each solution was distilled at different rates so that the effect of rate could be studied.

The System Chloroform-Toluene

The system chloroform-toluene was selected because a solution of these components is easily analyzed by determination of its specific gravity, the equilibrium diagram is accurately known, and reasonably accurate latent heats and specific heats are known.

The latent heats of chloroform and toluene at their normal boiling points are 58.5 and 86.0 calories per gram, respectively. Kauffman gives the equation $C_t = 0.3834 - 0.001043t$ for the specific heat of liquid toluene. The specific heat for the vapor was taken as 0.320. Liquid chloroform has a specific heat of 0.238 and that of the vapor is 0.144. The latent heats at various temperatures for both liquids were calculated from these data (Table I). The latent heats, at the boiling point, of solutions of all compositions are shown in Figure 1.

Table I—Latent Heats of Chloroform and Toluene at Various Temperatures

Temperature C.	LATENT HEAT	
	Chloroform Cal./gram	Toluene Cal./gram
61	58.50	93.40
65	58.11	92.83
70	57.64	92.12
75	57.16	91.42
80	56.69	90.74
85	56.21	90.00
90	55.74	89.26
95	55.27	88.47
100	54.79	87.68
105	54.32	86.82
110	53.84	86.00

The compositions of liquid and vapor and the boiling points of solutions of chloroform and toluene as determined by Rosanoff² were used. Since the data were not complete it

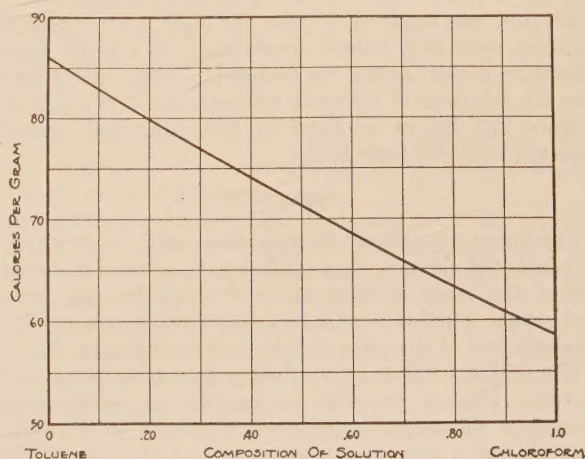


Figure 1—Latent Heats of Solutions of Chloroform and Toluene

was thought advisable to determine the equation of the curve passing through the known points. The equation is

$$y = \frac{x}{0.320 + 0.517x + 0.163x^2}$$

in which x is the composition of the liquid and y the composition of the vapor, both in terms of chloroform and expressed by weight as decimal parts of unity. At no point

¹ Received February 2, 1926.

² J. Am. Chem. Soc., 36, 1803 (1914).

does the curve represented by this equation deviate more than 0.2 per cent from the smoothest curve that can be drawn through Rosanoff's data. Table II gives the values of x and y as determined by the equation.

Table II—Values of x and y of the Vapor-Liquid Composition Curve for the System Chloroform-Toluene

x	y	x	y	x	y
0.000	0.000	0.350	0.672	0.700	0.918
0.050	0.143	0.400	0.724	0.750	0.937
0.100	0.268	0.450	0.768	0.800	0.955
0.150	0.372	0.500	0.808	0.850	0.970
0.200	0.465	0.550	0.842	0.900	0.981
0.250	0.542	0.600	0.871	0.950	0.991
0.300	0.612	0.650	0.896	1.000	1.000

Purification of Chloroform and Toluene

U. S. P. chloroform and toluene were used. Both liquids were fractionated twice, using a reflux ratio of approximately

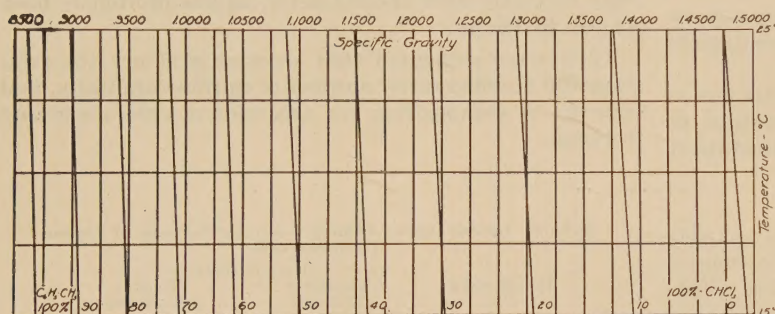


Figure 2—Specific Gravities of Solutions of Chloroform and Toluene between 15° and 25° C.

8. The first and last portions were necessarily discarded. The purified chloroform had a distillation range of 0.2° C. and the toluene 0.1° C.

Analytical Procedure

The analyses of the solutions were made by determining specific gravities with a Westphal type balance. An accuracy of ± 0.0003 was obtained with this instrument. Too much time was required to bring the liquid to the same temperature each time before determining its specific gravity. Therefore, a chart giving the change of density with temperature for solutions of different compositions was constructed (Figure 2). Errors involved in this analytical procedure were not over ± 0.1 per cent.

Apparatus

The apparatus (Figure 3) comprises a still, *A*, an insulated and jacketed column, *B*, a stillhead, *C*, where the temperature of the vapor is taken before it is divided into product and reflux, a reflux condenser, *D*, an orifice meter, *E*, for measurement of the reflux liquid, and a condenser, *F*.

The still is a 2-liter Pyrex flask with a bulb blown on the bottom. Heat is supplied by passing an electric current through a submerged resistance coil placed in the bulb so that all but a few cubic centimeters of the liquid can be vaporized.

The column consists of a 4-foot Pyrex glass tube 0.9 inch in internal diameter and jacketed by another glass tube. The tubes are lagged with 0.5 inch of asbestos paper. A galvanized iron jacket, *J*, is placed outside of the lagging, leaving an annular space 1 inch wide between the asbestos and the jacket tube. Air at the temperature of the still is blown into the lower end of the annular space. Thermometers are placed at regular intervals along the jacket so that the temperature of the annular space can be noted. The double glass tubing and lagging tend to minimize any heat exchange

with the outside resulting from slight variations of the temperature of the air in the jacket.

The volume of the column is 30.5 cubic inches. 5.6- and 6.5-mm. Lessing rings are used for column packing. The total weight of the small packing is 453 grams and that of the large packing 333 grams. The total surface area of the small packing is 687 square inches and that of the large packing 527 square inches. The sheet metal used to make the rings is 0.25 mm. thick.

The stillhead is a short glass tube to which are sealed the delivery tube and stopcock, *G*, through which the product makes its exit, and a side arm, *C*, through which the reflux liquid enters. The stopcock *G* is an ordinary one with a V groove filed on the inside of the male member. A pointer is fastened to the handle of the stopcock and moves over a dial so that the cock can be opened accurately to any desired extent. The vapor to be condensed and used as reflux liquid ascends through stopcock *H* to condenser *D*. A thermometer indicates the temperature of the vapor in the stillhead.

The flowmeter *E* consists of two concentric glass tubes. The reflux liquid from the condenser *D* flows into the annular space and through an orifice near the bottom of the inner tube and thence into the stillhead. The volume of liquid flowing through the orifice meter depends upon the temperature, composition, and height of liquid above the orifice.

With the apparatus described it is possible accurately to control the amount of reflux liquid. If stopcock *H* is closed and *G* opened there is practically no reflux. If stopcock *G* is closed and *H* opened there is total reflux. Any amount between no reflux and total reflux is obtained by adjusting stopcocks *G* and *H*.

Calibration of Flowmeter

In order to calibrate the flowmeter its lower end was disconnected from the apparatus and placed over a graduate. Stopcock *G* was closed, and chloroform put in the still and heated. The height of the liquid in the meter was read for various rates of distillation, thus giving a series of values. These are plotted in Figure 4. The calibration was made with chloroform alone since that liquid is the only one refluxed under ordinary conditions.

During fractionation there is some heat loss from the flowmeter, thereby cooling the reflux liquid below its boiling point. This cooling of the reflux liquid results in the condensation of chloroform in the stillhead. It was necessary to determine the quantity of reflux formed in this manner so that it could be added to the amount indicated by the flowmeter. The grams per minute to be so added for various flowmeter readings are shown in Figure 5.

Control of Jacket Temperature

In order to control the temperature of the jacket, thus making the column essentially adiabatic, air at the temperature of the boiling solution in the flask was forced into the

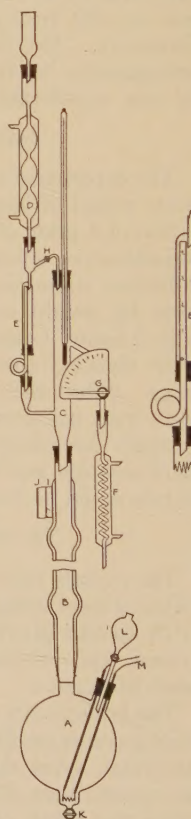


Figure 3—Distillation Apparatus

lower end of the annular space. Some of the air was allowed to escape through holes in the jacket so as to get the proper temperature gradient along the column. The correct temperature gradient was obtained by assuming that the column was working under equilibrium conditions and that the equilibrium units were of equal length. Both of these assumptions proved to be justified. Compositions and corre-

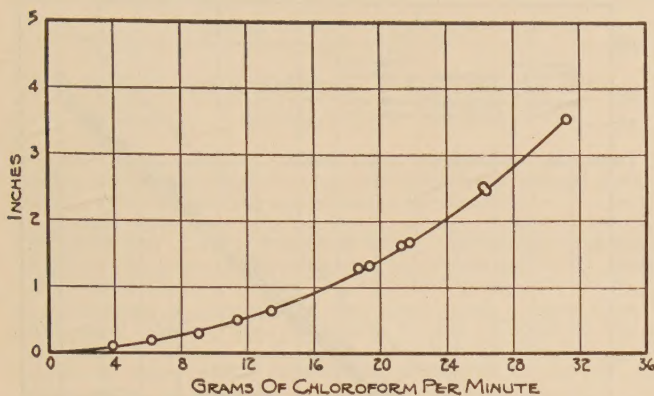


Figure 4—Flowmeter Calibration Curve

sponding temperatures in a typical instance are shown in Figure 6.

Thermal Efficiency of the Apparatus

In order to make corrections for heat losses it was necessary to determine the thermal efficiencies of all parts of the apparatus.

Since the still was kept over 80 per cent full at all times, practically all of the heat loss in the still was through the liquid, and there could have been little fractionation by dephlegmation. The thermal efficiency of the still was determined by disconnecting the flask from the rest of the apparatus and connecting it directly to an ordinary condenser inclined so that the product could be collected in a graduate. Eighteen hundred to two thousand cubic centimeters of the solution were placed in the flask and the current passed. Voltmeter, ammeter, and graduate readings were taken for several rates of distillation. The total or gross heat input was calculated from these data.

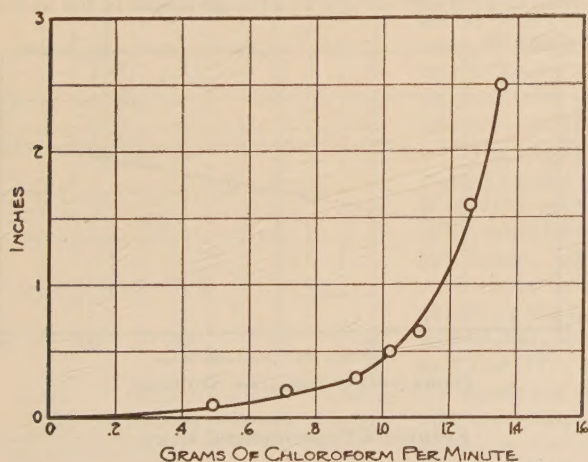


Figure 5—Flowmeter Correction for Cooling of Reflux Liquid

The difference between the heat loss in the still and the total heat input was called the net heat input because it was the actual amount of heat causing vaporization. The net heat input was obtained by multiplying the number of grams of

condensate by the latent heat at the temperature of ebullition. Gross and net heat inputs were determined for solutions containing 15, 25, 35, 50, and 100 per cent chloroform. The results, expressed in watts per second, are shown in Figure 7.

To prove whether or not the column was adiabatic the stillhead was replaced by an ordinary condenser, the still and column being run as usual. It was found that the heat loss was the same as when the still was used alone. The column therefore functioned adiabatically.

As may be seen in Figure 3, the product and reflux were taken directly from the stillhead. Since the product was practically pure chloroform, the vapor in the stillhead was also all chloroform. Obviously, all of the heat loss in the stillhead resulted in the condensation of chloroform that then acted as reflux liquid. In order to ascertain the quantity of this stillhead reflux, it was necessary to determine the heat loss from the stillhead. In order to do this the apparatus was assembled, stopcock *H* closed, the flask filled with chloroform, and the current passed through the heating coil. The heat loss in the stillhead was calculated by subtracting the heat loss in the still from the total heat loss. The losses in watts per second for various net heat inputs are shown in Figure 8.

Method of Operating the Apparatus

The operation of the apparatus was complicated by the fact that it was necessary to control and synchronize two independently variable conditions—namely, the weight of reflux per unit weight of product and the instantaneous composition of the liquid in the still.

The solution of chosen composition was placed in the flask, the electric heating circuit closed, and hot air blown into the jacket. Stopcock *G* was closed so that there was total reflux. The required change in composition was at first obtained in the lower part of the column while the

upper part was not functioning because a minimum number of equilibrium units were required when the reflux was total. Under those conditions the whole column was at a lower temperature than the jacket. If stopcock *G* was opened to the required extent, and 25 cc. of product collected, the column walls and packing would change temperature rapidly as a result of changing phase composition within the column. During this period of adjustment chloroform would condense because the temperature of the column walls and packing would be gradually increased to the equilibrium temperature corresponding to the state at which final readings were to be taken. Obviously, experimental readings taken under such conditions would not be correct. To rectify this state of affairs an extra 200 cc. of chloroform was added to the solution in the still. When the column was thoroughly heated, stopcock *G* was opened to the required extent and the 200 cc. of chloroform collected, thus bringing the composition of the liquid in the still to that desired. If the next 25 cc. collected as product was substantially pure chloroform, but the second 25 cc. contained some toluene, it is obvious that the reflux ratio during the collection of the first 25 cc. was the lowest that

Composition Per cent chloroform	Tem- perature °C.
100.00	61.2
99.5	61.4
98.2	61.8
95.8	62.8
91.6	64.5
85.9	66.9
78.2	70.1
70.8	73.4
62.2	77.6
54.8	81.4
50.0	83.8

Figure 6—Composition and Temperature Gradients along Column in a Particular Instance

allowed the production of pure chloroform. If the first 25 cc. contained some toluene there was not enough reflux. The experiment then had to be repeated with stopcock *G* more nearly closed. If both 25-cc. samples were practically pure chloroform the reflux ratio was too great. It was then necessary to repeat the experiment with the stopcock opened more.

During the determinations readings were taken of the current flow in the heating coil, voltage drop across the heating coil, temperature of the vapor as it left the stillhead, head of liquid in the flowmeter, barometric pressure, and the time required for the collection of 25 cc. of product. Table III shows the data taken during one determination.

Table III—Data Taken in Each Experiment

Composition of still liquid, 0.50 per cent chloroform		
	Initial	Final
Current, amps.	4.43	4.43
Voltage	52.0	52.0
Temperature	60.8° C.	61.0° C.
Flowmeter	0.83 inch	0.82 inch
Barometric pressure	734 mm.	
Time	92 seconds	
Dial	2.0	

Typical Method of Calculating Results

Q_s , the heat required per gram of product, equals the net heat input per minute divided by the weight of product collected in one minute. The total watts supplied equals volts times amperes, or $52.0 \times 4.43 = 231$. By reference to Figure 7 it is seen that 231 gross watts correspond to 173 net watts for a solution whose composition is 50 per cent. The rate of product separation is 23.9 grams per minute. The heat required per gram of product is:

$$Q_s = \frac{173 \times 0.24 \times 60}{23.9} = 104 \text{ calories}$$

V_s , the grams of vapor required for the separation of 1 gram of product (vaporization), equals the net heat input per minute divided by the latent heat per gram of the vapor and by the weight of product separated per minute. From Figure 1 the latent heat of the vapor (0.808 CHCl_3) in equilibrium with the liquid (0.500 CHCl_3) in the still is seen to be 62.8 calories per gram. Then

$$V_s = \frac{173 \times 0.24 \times 60}{62.8 \times 23.9} = 1.657 \text{ grams}$$

L_R , the weight of reflux liquid per gram of product (reflux ratio), may be calculated in two ways. The first method is by the use of thermal equivalents. Since the column is adiabatic all toluene that vaporizes in the still must vaporize a thermally equivalent weight of chloroform during the process of countercurrent contacting in the column. Therefore, all heat put into the column may be expressed directly as grams of chloroform leaving the top of the column. All of the chloroform not collected as product is returned to the top of the column as reflux. Therefore

$$L = \frac{\text{heat input per minute}}{\text{latent heat of chloroform}} - \text{grams of product per minute}$$

$$L_R = \frac{\frac{173 \times 0.24 \times 60}{58.5} - 23.9}{23.9} = 0.78 \text{ gram}$$

The second method of calculating the weight of reflux liquid consists in totaling the following quantities:

- (1) Weight of liquid corresponding to the flowmeter reading
- (2) Weight of chloroform condensed in stillhead due to cooling of the reflux liquid in the flowmeter
- (3) Weight of chloroform condensed in the stillhead as a result of heat loss in that part of the apparatus

Referring to Figure 4, 0.825 inch head of liquid in the flowmeter corresponds to 15.1 grams of reflux per minute. The heat loss in flowmeter is equivalent to 1.2 grams of reflux (Figure 5). Also, 1.9 grams of chloroform are condensed per minute in the stillhead. The last quantity is obtained from the curve in Figure 8. The sum of these three quantities,

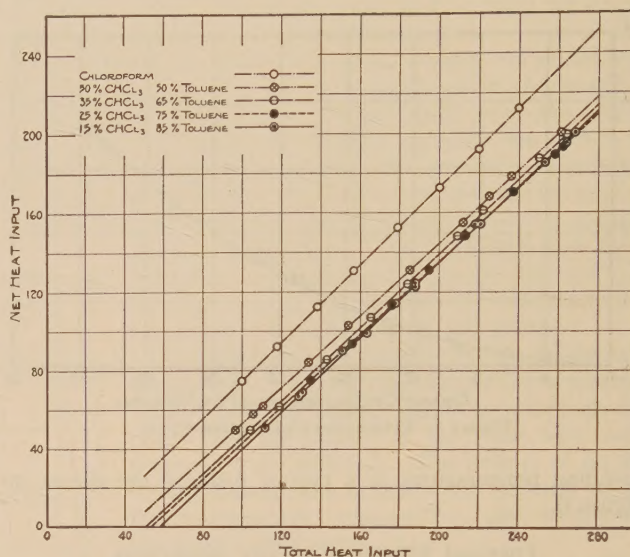


Figure 7—Thermal Efficiency of the Distillation Flask

or the total reflux, divided by the rate of product formation equals the reflux ratio. Hence

$$L_R = \frac{18.2}{23.9} = 0.76 \text{ grams}$$

The excellent agreement between the values of L_R calculated by these two methods illustrates how closely it is possible to work. It also shows that the column really functions adiabatically.

The number of equilibrium units (as from data in Table III) represented by the column under the above conditions may be found by ascertaining the intersection of the iso-reflux ratio line 0.77 and the abscissa $C_{LN} = 0.500$ in Figure 12, and by reading the corresponding ordinate. The value is approximately 9; that is, there are nine equilibrium units in the column, each unit having an average length of 5.3 inches.

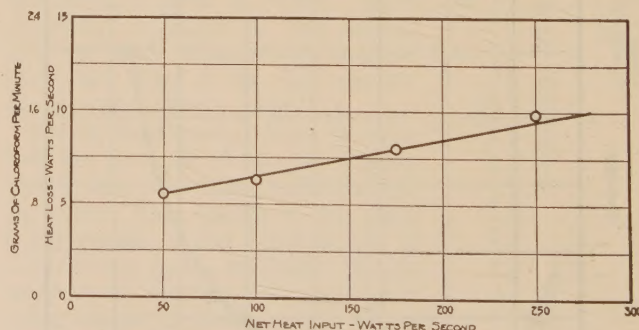


Figure 8—Heat Loss from Stillhead

Results of Experimental Work

As stated at the outset of this paper, one object of the work was to compare the performance of the column with that of the hypothetical column of infinite number of sections and minimum vaporization and reflux ratios. In order to do this use has been made of the following equations³ for the

Leslie, "Motor Fuels," p. 87.

calculation of the quantities pertaining to the hypothetical column:

$$V'_s = \frac{L_P(C_{LP} - C_{LS})}{C_{VS} - C_{LS}} \quad (1)$$

$$Q'_s = V'_s [h_b C_{VS} + h_a(1 - C_{VS})] \quad (2)$$

$$L_R = \frac{V_S[C_{VS}(h_b - h_a) + h_a]}{C_{LP}(h_b - h_a) + h_a} - L_P \quad (3)$$

$$\Delta C_{LN} = \frac{V_N(C_{VN} - C_{LN}) - L_P(C_{LP} - C_{LN})}{V_N - L_P} \quad (4)$$

$$V_N = \frac{(L_R + L_P)[C_{LP}(h_b - h_a) + h_a]}{C_{VN}(h_b - h_a) + h_a} \quad (5)$$

In these equations C stands for a composition expressed in terms of the more volatile component and as a decimal part of unity. Units of weight and not mols are meant.

Except when used as subscripts, L always stands for a weight of liquid and V for a weight of vapor. Subscripts of L or V indicate the point in the apparatus where the particular weight of liquid or vapor is located.

Subscripts of C consist of two parts—first, a letter L or V indicating whether the composition is that of liquid or vapor; and second, letters, S , N , R , P , indicating the location of the liquid or vapor whose composition is referred to, as still, n th plate, reflux, or product.

Symbols h_a and h_b stand for the latent heats of vaporization per unit weight of substances A and B , respectively. B is the more volatile component.

The mark ', or "prime," indicates that the quantity so marked is the minimum.

Symbol ΔC stands for an increment of change in composition from one point in the column to the next.

Q_s represents the heat input to the still per unit weight of product.

Heat Required per Gram of Product

The minimum heat required for the separation of 1 gram of almost pure—that is, 99.98 per cent—chloroform in the hypothetical column of infinite number of equilibrium units was calculated by use of Equations 1 and 2. The quantity

within the parenthesis of Equation 2 can be read directly from Figure 1.

Figure 9 serves to compare the calculated heat requirement of the hypothetical column with the actual heat requirement of the laboratory column when packed with either 5.6-mm. or 6.5-mm. Lessing rings. The requirement of the laboratory apparatus is corrected for radiation losses. The per cent excess heat required by the laboratory column is shown in Table IV. When the separation is easy little more heat is required by the laboratory column than by

the ideal column, but as the separation becomes more difficult, or as the effectiveness of the column is reduced by increasing the size of the packing, the excess heat increases rapidly. This excess heat is the price that must be paid because the laboratory column comprises a finite number of

equilibrium units, approximately eight in the column with 5.6-cm. ring packing, rather than the infinite number of the hypothetical column.

Table IV—Heat Required per Gram of Product

C_{LN}	Hypothetical column Cal./gram	Lab. column Av. cal./gram	Excess heat required by lab. column Per cent
5.6-Mm. Ring Packing			
0.500	101.9	104.9	3
0.350	134.0	144.8	8
0.250	180.0	202.0	12
0.150	287.0	354.4	23
6.5-Mm. Ring Packing			
0.500	101.9	122.0	20
0.250	180.0	224.7	25

Weight of Reflux per Gram of Product

The weight of reflux liquid required per gram of product by the column of infinite number of equilibrium units—that is, the minimum reflux—was calculated by use of Equation 3. The latent heats used in the numerator must be those corresponding to the

temperature at which the vapor is formed in the still, and the value of h_b used in the denominator must be that corresponding to the boiling point of chloroform.

Figure 10 presents curves showing the minimum reflux and also the actual reflux required by the laboratory column when packed with 5.6- and 6.5-mm. rings and when producing 99.98 per cent chloroform. The per cents excess reflux shown in Table V are larger than the per cents excess heat shown in Table IV, mainly for the reason that they are based on the weight of reflux in the one case and on the approximate thermal equivalent of the weight of reflux plus unit weight of product in the other. Also, Equation 3 is approximate in that it does not take sensible heat quantities into account.

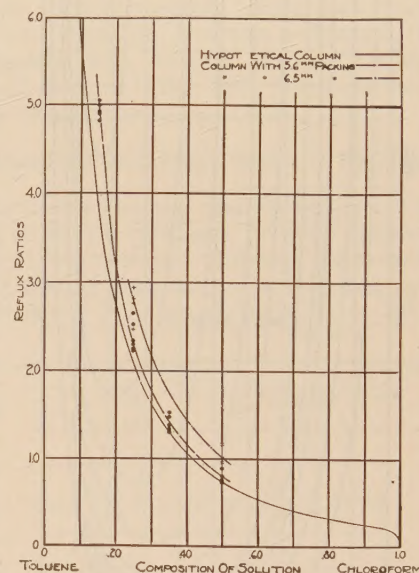


Figure 10—Comparative Reflux-Ratio Requirements of Laboratory Columns and Hypothetical Column

Table V—Weight of Reflux per Gram of Product

C_{LN}	Minimum reflux Grams/gram	Lab. column actual reflux Grams/gram	Excess reflux Per cent
5.6-Mm. Ring Packing			
0.500	0.074	0.79	7
0.350	1.29	1.42	10
0.250	2.08	2.39	15
0.150	3.91	4.94	26
6.5-Mm. Ring Packing			
0.500	0.74	1.05	42
0.250	2.08	2.78	34

Fractionation Characteristics of System $\text{CHCl}_3\text{-C}_6\text{H}_5\text{CH}_3$ and Determination of Equilibrium Units in Laboratory Column

The problem of calculating the number of equilibrium units required to effect the separation of 99.98 per cent chloroform from a solution of any given concentration, when operating with any given weight of reflux liquid per unit

weight of chloroform, can be solved by the use of Equations 4 and 5.

If it is desired to generalize the problem so that the number of equilibrium units required when any reflux ratio is used and a solution of any concentration is distilled, this can be done by constructing a series of integral curves of $\frac{1}{\Delta C_{LN}} C_{LN}$

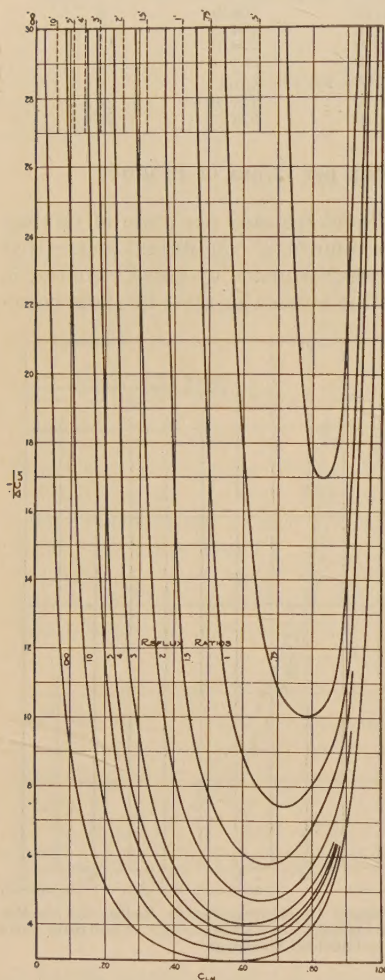


Figure 11—Integral Curves of $\frac{1}{\Delta C_{LN}} C_{LN}$

11 are to be preferred. These are shown as Figure 12. The number of equilibrium units required to effect the separation of a product of any possible composition from a solution of any concentration, when operating with any reflux ratio, can be read from this diagram.

Several interesting facts are disclosed by inspection of Figure 12. For example, when distilling a solution of some given composition, increase of reflux ratio at first has a large effect, but a point is soon reached from which any further increase is of little benefit in reducing the number of equilibrium units required. Likewise, it is evident that for a particular reflux ratio there is at first a great increase in the fractionating ability of a column as the number of equilibrium units is increased, but a number of units is soon reached beyond which the addition of even a very large number of units does little in the way of increasing the fractionating ability of the apparatus as a whole. For the accomplishment of any particular fractionation there is an optimum range of reflux ratio and number of equilibrium units, the exact choice rest-

ing on the relative cost of heat and overhead charges on investment.

In this investigation the writers were interested in determining the number of equilibrium units in the column when packed with 5.6-mm. and with 6.5-mm. Lessing rings. With Figure 12 at hand this is easily accomplished. A point is located representing the intersection of the vertical line passing through the abscissa corresponding to the particular C_{LN} and the iso-reflux line corresponding to the reflux ratio as determined by measurement during the experiment. Projection from this point to the equilibrium-unit axis gives the number of units directly. The H. E. T. P.'s mentioned in another section of this paper were found in this way.

Effectiveness of Column as Affected by Vapor Velocity

An important question that arises in connection with the design and operation of distilling columns is the influence of vapor velocity on the effectiveness of the column. That is, if a solution of given concentration is being distilled, and the reflux ratio is constant, will the column operate as well at high vapor velocity as at low? Furthermore, if it is found that distillation rate is without important effect at high reflux ratio, is this true also for low reflux ratio?

Peters⁵ states that in distilling solutions of acetic acid and water the plate efficiency of a sieve-plate column was constant for values of ρ between 0.8 and 1.0. ρ is defined as $\frac{\text{heat in reflux}}{\text{total heat in vapor}}$, or, in our nomenclature, $\frac{L_R}{L_R + L_P}$. Al-

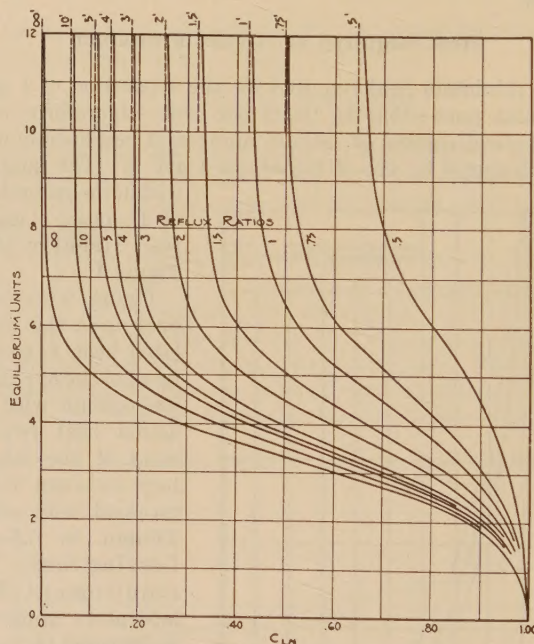


Figure 12—Equilibrium Units Required to Effect Any Separation of Chloroform and Toluene at Various Reflux Ratios

though the point is not mentioned, Peters presumably meant that the reflux ratio was constant. However, values of 0.8 to 1.0 for ρ are equivalent to reflux ratios between 4.0 and ∞ . For the particular solution distilled this is the range of high reflux ratio—that is, the range in which a change in reflux ratio would make little difference in the fractionation effected by a particular column. Consequently, it is entirely possible that the plate efficiency for values of ρ between 0.8 and 1.0 would be substantially constant and independent of reflux ratio as well as of vapor velocity, whereas, at lower values

⁴ "Motor Fuels," p. 97.

⁵ THIS JOURNAL, 14, 477 (1922).

of ρ , the constancy of plate efficiency at various vapor velocities might hold only at constant reflux ratio. In passing, it should be noted that high reflux ratio for the distillation of one solution may be low reflux ratio for another. It all depends on how easily the components are separated.

Calingaert and Huggins⁶ studied the exhaustion of ammonia-water solutions in a coke-packed column and drew the conclusion that "the efficiency of the still investigated was proportional to the reflux at constant vapor velocity, or inversely proportional to the vapor velocity at constant reflux." The present writers' findings are not in agreement with these conclusions. In fact, they are such as to indicate that the effectiveness of a packed column is not affected by vapor velocity within the range of conditions investigated. In Table VI data to illustrate this point are presented.

Table VI—Relation of Effectiveness of Packed Column to Vapor Velocity and Reflux Ratio

Conditions	Expt.	Grams product per minute	Calories per gram product	Reflux ratio $\frac{L_R}{L_P}$	Vapor velocity Ft./sec.	H. E. T. P. Feet
$C_{LN} = 0.500$	1	15.9	110	0.90	0.41	0.45
$C_{LP} = 0.998$	6	24.7	106	0.80	0.60	
5.6-mm. packing	7	27.1	106	0.81	0.67	
$C_{LN} = 0.350$	8	11.2	143	1.39	0.36	0.45
$C_{LP} = 0.998$	10	14.8	149	1.49	0.50	
5.6-mm. packing	12	18.1	152	1.54	0.62	
$C_{LN} = 0.250$	13	9.0	200	2.35	0.41	0.56
C_{LP}	15	10.5	200	2.35	0.47	
5.6-mm. packing	19	12.4	218	2.66	0.62	
$C_{LN} = 0.150$	20	6.0	346	4.82	0.48	0.59
$C_{LP} = 0.998$				5.00	0.55	
5.6-mm. packing						
$C_{LN} = 0.500$	25	14.7	121	1.03	0.40	0.61
$C_{LP} = 0.998$	31	20.0	130	1.18	0.59	
6.5-mm. packing	32	22.7	129	1.17	0.67	
$C_{LN} = 0.250$	33	7.0	236	2.95	0.38	0.63
$C_{LP} = 0.998$	35	9.2	229	2.83	0.47	
6.5-mm. packing	38	9.8	225	2.77	0.50	

For each set of conditions the vapor velocities ranged from the lowest feasible to the highest that could be used without priming the column. At each reflux ratio the H. E. T. P. was unaffected by vapor velocity change. The reflux ratio range covered was 0.8 to 5.0, which is equivalent to values

of $H = \frac{\text{total heat}}{\text{heat in product}}$ of 1.8 to 6.0, or of $\rho = 0.44$ to 0.83.

Peters' work covered values of ρ from 0.8 to 1.0. Hence it appears that, for values of ρ between 0.44 to 1.0, and at any chosen but constant reflux ratio, the effectiveness of a packed column is not materially affected by a change in the velocity of the vapor. Since columns, particularly packed columns, will seldom be used with lower reflux ratios than 0.80, it follows that in practical work vapor velocity can be disregarded as a variable factor. It is here assumed, of course, that the velocity is not so high as to prime the column.

With regard to the effect of reflux ratio on the fractionating ability of column equipment, no conclusions can be drawn. The data in Table VI indicate an increase in the H. E. T. P. with increasing reflux ratio. This is more marked when using the smaller packing than when using the larger, which suggests that the effect observed has to do with fluid mechanics.

It will be noted that the data of Table VI and those of Calingaert and Huggins,⁶ as regards the effect of reflux ratio on the H. E. T. P., are directly opposed. More work must be done before any conclusions can be drawn. However, it appears entirely possible that, barring abnormal reflux distribution in packed columns, reflux ratio is without important effect on the effectiveness of the column.

Relation between Diameter and Effectiveness of Packing

Peters⁵ has presented data showing that the effectiveness of a particular form of column packing is inversely proportional to the diameter of the packing. Although the writers used only two sizes of packing, their results, as far as they go, confirm Peters' conclusion. They are shown in Table VII.

Table VII—Relation between Diameter and Effectiveness in Packing

Diameter of packing Mm	H. E. T. P., FEET		
	$C_{LN} = 0.500$ $L_R = 0.8 \text{ to } 1.0$	$C_{LN} = 0.250$ $L_R = 2.4 \text{ to } 2.8$	
5.6	0.45	0.56	
6.5	0.61	0.63	
Ratio $\frac{5.6}{6.5} = 0.86$	Ratio $\frac{0.45}{0.61} = 0.74$	Ratio $\frac{0.56}{0.63} = 0.89$	

⁶ THIS JOURNAL, 16, 584 (1924).

